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Method and Apparatus for the Manufacture of a Tube Made of Film on a Cellulose Basis Which Reinforces an Insert

The invention relates to a method and an apparatus for the manufacture of a tube made of film on a cellulose basis, which reinforces an insert, by extruding an aqueous solution of cellulose-N-methyl-morpholin-N-oxide (NMMO) onto the insert.

Cellulose is not soluble in common solvents and has neither a melting point nor a melting range and therefore cannot be worked as a thermoplastic. For this reason cellulose is normally converted chemically for the manufacture of casings for foods, such as sausage casings, this process involving a degradation of the cellulose, i.e., the average degree of polymerization of the cellulose is lower. Such methods are technically very complicated and accordingly expensive to practice.

Presently the viscose method is preferred in the extrusion of film tubes on a cellulose basis. The cellulose is reacted with caustic soda solution and then reacted with carbon disulfide. Thus, a cellulose xanthate solution is obtained, which is extruded through a spinning or ring nozzle into a so-called spin bath or coagulating bath. The cellulose is regenerated by means of additional coagulating baths and washing baths.

It has long been known that cellulose is soluble in oxides of tertiary amines, and that at present the most appropriate solvent for cellulose is N-methyl-morpholin-N-oxide (NMMO). The cellulose dissolves therein, without changing chemically. No breakdown of cellulose chains takes place. The preparation of appropriate spinning solutions is known (DD 218 104; DD 298 789; US-A 4,145,532, US-A 4,196,282, US-A 4,255,300).

Filaments can be made from the solutions by extrusion into a spin bath (DE-A 44 09 609; US-A 5,417,909). In WO 95/07811 (= CA 2,149,218) there is also

disclosed a method for the preparation of cellulose tubular films by the aminoxide method. What is distinctive of this method is the cooling of the extruded film with a cooling gas immediately under the ring gap of the extrusion nozzle. According to EP A 662 283, the extruded tubular film is cooled from within by a liquid.

Recovery and purification of the NMMO are described in DD 274 435. Since the cellulose is not chemically converted in the process the apparatus cost is lower. In the aminoxide method no gaseous or aqueous waste products are produced, so that there are no problems with exhausts or waste water. It is therefore acquiring increasing importance.

In EP-A 0 686 712 the production of flexible cellulose fibers by the N-methylmorpholin-N-oxide (NMMO) is described. In it a cellulose solution in aqueous NMMO is forced through a spinneret, carried across an air gap into an aqueous coagulating bath containing NMMO and then washed, finish-treated and dried.

According to WO 93/13670 a seamless, tubular food casing is made by extruding a solution of cellulose in NMMO/water by means of a special extrusion die. Between the extrusion die and the coagulating bath there is an air gap. Distinctive of this method is an especially formed hollow mandrel through which the coagulating liquid can circulate also inside of the tube. In the air gap the interior of the extruded tube is filled virtually completely with the hollow mandrel and the coagulating liquid. The tube is not stretched transversely.

In WO 95/35340 a method is described for the production of cellulose blowing films in which a non-derivatized cellulose dissolved in NMMO is used.

In the state of the art, methods and apparatus are known for the production of a fiber-reinforced cellulose tube by the viscose process, but these methods and apparatus are not applicable in NMMO technology for the following reasons:

- Different temperatures of the spinning solutions
- Different viscosities of the spinning solutions
- Different solvents
- Different sensitivities to evaporation and dilution, temperature fluctuations, and different temperature limits.

Usually the cellulose in the viscose process is spun in the temperature range of 20 to 45°C. Instead, the extrusion temperature of cellulose NMMO solutions is around 85 to 115°C,

The viscosity of cellulose in the viscose process is about 10 to 30 Pas, and that of NMMO solutions 10 to 300 Pas, especially 20 to 200 Pas. Cellulose in the viscose process reacts with caustic soda solution and then with carbon disulfide, while the NMMO solutions are organic solutions.

The invention is therefore addressed to the problem of designing a method and an apparatus so that they are suitable for coating inserts formed into a tube with cellulose-NMMO solutions and permit a uniform penetration of the inserts with cellulose-NMMO solutions.

This problem is solved as regards process in that the insert is drawn from a supply roll, treated with emulsifiers, wetting agents and/or anchoring agents and formed into a tubular envelope with an overlapping longitudinal seam which is cemented ahead of a nozzle block through which the envelope is carried and in which the cellulose-NMMO solution is applied to the envelope and

penetrates it in order to obtain an insert-reinforced film tube, that the interior of the film tube is filled with an aqueous NMMO solution, and that the film tube exits from the nozzle block and enters into a spinning bath, turned about in the latter and carried out of it.

In embodiment of the process, the tubular envelope passes through a heating section ahead of the nozzle block, in which it is preheated with hot air to the temperature of the extruded cellulose-NMMO solution. A controlled-pressure supporting air is blown into the interior of the film tube after it leaves the nozzle block

As the process continues, the film tube is carried through a heated annular gauging disk through which a heating medium flows in a controlled circuit.

In embodiment of the process, aqueous NMMO solution is delivered into the interior of the film tube and also removed therefrom, the delivery and removal being performed at a distance apart from one another. At the same time the level of delivery of the aqueous NMMO solution in the film tube is adjustable and its removal is performed such that the level in the film tube is variably up to 20 mm higher and up to 45 mm lower than the level in the spin bath.

The rest of the process is to be found in the features of claims 7 to 12.

As a variant of this process it is also possible, instead of passing through a tub filled with the spin bath, to apply the spin bath directly internally and externally onto the film tube, through ring nozzles for example, as is described in EP-A

0 006 601. The spin bath level is then lowered inside and out to the top edge of the spin tub pulley.

The apparatus for the production of a film tube on a cellulose basis, which the insert reinforces, by extruding an aqueous cellulose-N-methyl-morpholin-N-oxide-(NMMO) solution onto the insert, with a nozzle block and a spin bath, is characterized in that a supply roll for the insert, a deflector roll with a device for applying additives to the insert carried from the supply roll over the deflector roll, a forming section in which the insert is shaped to a tubular envelope with overlapping longitudinal seam are present, that the tubular envelope passes through the nozzle block which is preceded by a cementing device for cementing the longitudinal seam of the tubular envelope and which contains a ring nozzle from the nozzle gap of which the cellulose-NMMO solution is extruded onto the tubular envelope to form a film tube, that between the exit from the nozzle block and the spin bath a temperature-controlled air section is present in a spin tub, that near the bottom of the spin tub a return roll for the film tube plunging vertically into the spin bath is disposed, and that a delivery and removal tube for the aqueous NMMO solution as well as a duct for supporting air are situated in the interior of the film tube.

In further embodiment of the invention the insert is selected from the group, paper, nonwoven, fiber mat and fiber paper, wherein the fibers are especially long hemp fibers. In addition, a system for preheating the tubular envelope is disposed ahead of the nozzle block and the preheating system is connected by hot air ducts and an exhaust line to a controllable heater out of which air heated in the circuit flows into the preheating system and from which cooled air flows back into the heater. It is also possible that the preheating system is not needed in every case, so that it remains shut off in certain production procedures. It is also conceivable that the apparatus according to the invention can be operated without any such preheating system.

In an embodiment of the invention, the nozzle block contains a ring nozzle which is heated by a heating medium and the infeed and outfeed tube and the duct for the air supporting the film tube are brought centrally through an annular calibration disk which is arranged concentrically with the ring nozzle in the interior of the film tube and forms with the latter an annular gap through which the film tube passes.

The annular calibration disk is connected with the heating circuit for heating.

In embodiment of the apparatus, the infeed tube and the outfeed tube are adjustable for height within the film tube.

The further configuration of the apparatus will be apparent from the features of claims 19 to 25.

By the method of the invention a substantially uniform penetration of the insert with the cellulose-NMMO solution, so that, after passing through additional treatment steps, such as precipitation or coagulation baths, a composite of a fiber-reinforced film tube is obtained which has improved properties for its use. The fiber-reinforced film tube on a cellulose-NMMO basis corresponds in its properties to the known cellulose fiber or fiber casings which are made from cellulose hydrate and reinforced with wet-strengthened fibers of cellulose (= cellulose fiber fleece).

The invention is further explained below with the aid of the drawings, wherein:

Fig. 1 is a schematic sectional view of the apparatus according to the invention with a height-adjusted infeed tube in the film tube.

Fig. 2 is a schematic sectional view of an apparatus similar to that of Fig. 1, with infeed tube lowered into the film tube;

Fig. 3 is an enlarged sectional view at point A in Fig. 1, and

Figs. 4a and 4b are side and top views of a cementing device for a tubular envelope, formed from an insert.

An apparatus 1 shown in Fig. 1 for extruding an aqueous cellulose-N-methyl-morpholin-N-oxide (NMMO) solution onto an insert comprises a supply roll 2 for the insert 3, a deflector roll 4, a shaping section 5, a nozzle block 7 with a ring nozzle and a spin tub 12 which is filled with a spinning or precipitation bath 11.

The insert 3, which is paper, nonwoven, fiber paper or fiber fleece wherein the fibers are preferably hemp fibers, is drawn from the supply roll 2 and carried over the deflector roll 4. The fiber paper and the fiber fleece are solidified wet when manufactured, by being impregnated with dilute viscose, cellulose acetate solution or plastic washes. In these embodiments the insert 3 is used with preference. Ahead of the deflector roll 4 is an applicator 31 comprising a grid cylinder 32, a squeegee 33 and a pair of pinch rolls 34-35 for the application of additives, such as emulsifiers, wetting agents or sticking agents, to the insert 3. After the insert 3 passes over the deflector roll 4 the formation of a tubular envelope 6 with an overlapping longitudinal seam 38 (see Fig. 4a) takes place in the shaping section 5 by means of a forming shoulder not shown.

The tubular envelope 6 and the tube 10 which it forms is made by a vertically descending spinning. For this, the envelope 6 passes through the ring nozzle 21 in the nozzle block 7 through the gap of which the cellulose-NMMO

solution is extruded onto the envelope 6 to complete the formation of the film tube 10. First the longitudinal seam on the envelope 6 is cemented ahead of the nozzle block 7 by a cementing system 25 shown more in detail in Figures 4a and 4b; straight NMMO or cellulose-NMMO solutions serve as the adhesive at temperatures between 15 and 110°C, especially the temperature of the cellulose-NMMO solution that is to be applied.

The extruded cellulose-NMMO solution coats and penetrates uniformly through the tubular envelope 6. The pressure required for penetration is built up by the geometry of the annular gap 26 in the nozzle body 7, which amounts to 0.1 to 5 mm, especially 0.5 to 1.5 mm. The annular gap 26 is formed by a gauging disk 8 and the inside of the annular nozzle 21.

After exiting from the nozzle body 7 the film tube 10 passes through an air section 9 before it plunges into the spin bath 11 in the spin tub 12. In the air section 9 a temperature treatment with temperature-controlled air can take place if necessary, in which case heated air delays the solidification of the cellulose-NMMO solution and cool air accelerates it.

Instead of the one-sided application of the cellulose-NMMO solution to the outside of the envelop 6, the cellulose-NMMO solution can also be applied bilaterally, i.e., both to the outside and to the inside of the envelope 6.

The ring nozzle 21 serves as the outer ring nozzle, while the inner ring nozzle takes the place of the gauging disk 8 in Figures 1 and 2. The inner ring nozzle is, like the gauging ring disk 8, heatable. In this variant of the treatment, the outer and inner cellulose-NMMO solution filmcan be applied spaced apart from one another, i.e., delayed in time.

The spin bath 11 consists of an aqueous NMMO solution with an NMMO content 5 to 50 weight-percent, especially 8 to 20 weight-percent. A preheating system

15 is arranged in front of the nozzle block 7 and connected to a controlled heater 17 by hot air ducts 22 and 23 and an exhaust duct 24. The aqueous spinning solution extruded from the ring nozzle 21 is a cellulose-NMMO solution with a morpholine content of 75 to 90 wt.-%, especially 87.7 wt.-%. The spinning solution is fed on one side into the ring nozzle 21 by means of a spinning pump, not shown, and distributed in a largely uniform manner over the circumference through a nozzle gap through a distributor plate, not shown. The ring nozzle 21 has a double jacket 32 for heating the ring nozzle 21 to the temperature of the morpholine solution, a heating medium being provided for the purpose, which flows through the double jacket 32 and is heated in a controlled heating circuit 16 which is connected by lines to the double jacket 32. The film tube 10 extruded from the nozzle block 7 passes through the air section 9 in which it is expanded by compressed air and stretched slightly crosswise. The expanded film tube 10 has no contact with the outside of a tube 29 which extends downward past the bottom of the nozzle block 7. The air section amounts to 1 to 1000 mm, especially 200 to 500 mm. The tube 29 surrounds an inlet and outlet tube 18 and 19, respectively, for an internal bath solution 31 which fills the film tube 10. This internal bath solution is an aqueous NMMO solution with an NMMO content of 5 to 50 wt.-%, especially 8 to 20 wt.-%. The inlet and outlet tubes 18 and 19 extend vertically downward into the film tube 10 plunging into the spin bath 11. As the feeding of the internal bath solution 31 into the film tube 10 begins, the inlet tube 18 assumes a raised position, as shown in Fig. 1. As soon as the film tube is filled with the internal bath solution, the inlet tube 18 is advanced to a position in the film tube 10 which is just above the deflector roll 13 for the film tube 10, as can be seen in Fig. 2. The inlet tube 18 can be raised and lowered within the vertically plunging film tube 10, and so can the outlet tube 19.

Air at a pressure of 0.1 to 10 mbar above atmospheric is passed through a line 20 for supporting air into the interior of the film tube 10. This pressure produces a slight

expansion of the inflated film tube in the air section 9 directly following its exit from the nozzle block 7. The film tube 10 plunging into the spin bath 11 is turned around near the bottom of the spin tube 12. A deflector roll 13 is provided, which is power-driven, and around which the film tube 10 is passed. After the film tube turns around it is brought up through the spin bath 11 and out of the bath at an angle. The film tube 10 running upward at an angle is pinched together by the spin bath pressure just underneath the surface of the spin bath and is driven in the flattened state out of the spin bath 11. Wipers 14 on both sides of the collapsed film tube 10 wipe away the excess spin bath solution. The width of the flattened film tube 10 is kept as constant as possible. Any departure of the width of the flattened film tube 10 from the desired dimension results in a readjustment of the tension applied to the film tube in order to maintain the specified dimension.

Fig. 2 differs from Fig.1 only in that the inlet tube 18 is inserted so far down into the vertically descending film tube 10, in comparison to Fig. 1, that the mouth of the inlet tube is situated just above the deflector roll 13. The spin bath 11 and the internal bath solution31 are, as mentioned previously, aqueous NMMO solutions which, as the extrusion of the film tube 10 begins, have the same NMMO concentration. As extrusion progresses, the NMMO concentration of the inner bath solution 31 will increase, since morpholine penetrates the insert 3 during the cellulose regeneration, and enters into the internal bath solution 31 and concentrates therein. Since morpholine has a greater density than water, the concentration or density of the NMMO solution increases toward the deflector roll 13 inside of the film tube 10. The concentration of the NMMO solution in the spin bath 31 varies hardly at all, since the morpholine yielded by the film tube to the spin bath 11 can increase the NMMO concentration of the spin bath 11 to only a negligible

degree. In the inside bath solution 31 in the film tube 10, unless the NMMO concentration in the inside bath solution 31 is regulated, different coagulation conditions might occur, as well as a variation of the diameter of the film tube 10. Due to the constant delivery and removal of the inside bath solution 31 through the delivery and removal tube 18 and 19, respectively, a constant renewal of the inside bath solution 31 occurs, i.e., the inside bath solution 31 enriched with morpholine near the deflector roll 13 is diluted, so that the NMMO concentration of the inside bath solution 31 near the deflector roll 13 is less than or at most equal to the NMMO concentration of the spin bath 11. The tension applied to the film tube 10, together with thepressure of the spin bath 11, is enough to urge the film tube 10 against the deflector roll 13 along the line of contact 27 so that it is more or less flattened, as can be seen in Figures 1 and 2. Thus, uniform pressure conditions are established in the film tube over the entire length from just beneath the surface of the spin bath 11 to an area close to the deflector roll 13, so that the gauge or diameter of the film tube 10 is constant and shows no fluctuation or narrowing. The density of the inside bath solution 31 is thus dependent upon the throughput of the inside bath solution or morpholine solution, the amount of the inside bath and the depth of immersion of the inlet tube 18 or the point at which fresh morpholine solution is fed into the inside bath solution. The position or point at which the inside bath solution 31 flows into the film tube 10 substantially influences the gauge constancy, the level of the inside bath in the ascending film tube 10 after the deflector roll 13 and the location for the removal of the inside bath solution 31 from the interior of the film tube.

Fig. 3 shows on an enlarged scale the section indicated at A in Fig. 1. The tube 29 is lowered about 50 to 100 mm into the inside bath solution in the film tube. The aspirating tube 19 is in a position in which it establishes a level 30 inside of the tube 29, which is up to 20 mm higher or 45 mm lower than an inside bath level 28 of the inside bath solution of the film tube 10.

In other words, this means that the aspirating tube 19 assumes a position at which the inside bath solution is drawn up to a distance of as much as 20 mm higher or 45 mm lower than the tube level 28. The highest and the lowest tube levels 30 are indicated by broken lines 30_{max} and 30_{min} in Fig. 3. The aspiration usually starts below the level of the spin bath 11, so that the air section 9 situated above it and the pressure conditions there prevailing have no influence on the inside bath solution and thus cannot produce any gauge fluctuations in the film tube 10, either. If the aspiration is performed above the level of the spin bath 11, the effect of the pressure conditions in the air section 9 on the film tube 10 is negligible, since the latter is made stable in shape by the insert to the extent that it is hardly subject to any gauge variations.

Due to the adjustment of the depth of immersion of the inlet tube 18 and the constant renewal of the inside bath solution the density of the inside bath solution 31 is kept at a uniform level, which results in a constriction of the film tube 10 along the line of contact 27 with the deflector roll 13 and keeps the level of the inside bath solution 31 in the ascending film tube 10 constant for as long as desired with respect to the surface of the spin bath 11, so that irregular running and film tube gauge variations no longer occurs. The constant renewal and the minimum delivery of inside bath solution 31 are to be determined individually for each rate of extrusion or output of the film tube.

The film tube 10 emerging from the spin bath 11 then passes through precipitation and washing tubs not shown, and can also be treated with plasticizers, for example, and then dried before being wound up and further treated.

In a variation of the method, the level of the spin bath 11 inside and outside of the film tube is lowered to the upper edge of the deflector roll 13

and the film tube 10 can be sprayed inside and out with the spin bath through ring nozzles, as described, for example, in EP-A 0 006 601.

In Figures 4a and 4b, a side view and top view of the cementing system 25 are shown schematically. The cementing system 25 comprises a hollow, fixed finger 36 with a slit 37 from which the cement flowing inside of the finger 36 is applied to the longitudinal seam 38 of the tubular envelope 6. The envelope 6 is simultaneously moving vertically in the direction of the arrow to the finger 36.

The film tube 10 can be expanded alternatively or additionally to the supporting air through a tube, a ring or a spreader in flat form, free of wrinkles.

Besides the treatment of the film tube 10 in the spin bath 11, as described in Figures 1 to 4b, with complete immersion of the film tube in the spin bath, wherein the tube interior is filled with an inside bath for pressure equalization, and the inside bath level 28 can be regulated differently from the tube level 30 in the tube 29 or by the outside level of the spin bath 11, it is also possible, in the case of the previously described bilateral coating with cellulose-NMMO solution, a film of NMMO solution can be applied to the outside as well as to the inside of the film tube 10 by means of an outer and inner annular ring nozzle.